

RESERVE COPY
PATENT SPECIFICATION

NO DRAWINGS

1,124,911

1,124,911



Date of Application and filing Complete Specification: 4 Jan., 1966.
 No. 237/66.

Application made in Germany (No. B79984 IVc/39b) on 5 Jan., 1965.
 Complete Specification Published: 21 Aug., 1968.
 © Crown Copyright 1968.

Index at acceptance: —C3 G(1BX, 1C2, 2B, 2C, 3A2, 3C4, C)

Int. Cl.: —C 08 f 25/00

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:— HERBERT WILLERSINN, HANS-WERNER OTTO, PAUL RAFF and LUDWIG SCHUSTER, citizens of the Federal Republic of Germany, residing, respectively, at 98 Erzbergerstrasse, Ludwigshafen/Rhein; 161 Sternstrasse, Ludwigshafen/Rhein; 10 Ottweiler Strasse, Ludwigshafen/Rhein; and 9 Alwin-Mittasch-Platz, Ludwigshafen/Rhein; all Federal Republic of Germany.

COMPLETE SPECIFICATION

Impact Resistant Moulding Materials

- We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
- 5 This invention relates to impact resistant moulding materials based on copolymers of styrene and acrylonitrile and elastomeric acrylic ester polymers which are compatible with styrene/acrylonitrile copolymers. 40
- 10 Polymers based on styrene or copolymers of styrene and acrylonitrile have been known for a long time. Polystyrene and copolymers of styrene and acrylonitrile are crystal clear and the polymers of styrene/acrylonitrile have a good surface hardness. Both types of polymer are however lacking in shock resistance. They are not impact resistant and mouldings made from these polymers may break under severe stress. 45
- 15 It has been known for a long time that soft elastomeric polymers may be incorporated into these hard and brittle polymers and copolymers in order to achieve impact resistance. Transparency is, of course, lost in the process. To achieve homogeneous mixtures of elastomeric components with the hard and brittle polymer based on styrene or styrene/acrylonitrile, it is necessary for the soft and hard components to be compatible with one another. To achieve this compatibility, various proposals have already been made. Thus the elastomeric soft components have been grafted with styrene or styrene/ 50
- 20 Natural or synthetic rubbers have been used as elastomeric components in prior art production of impact resistant polystyrenes or so-called ABS polymers. In particular homopolymers and copolymers of butadiene have been used as synthetic rubbers for this purpose. Elastomeric polymers which contain little or no double bonds, particularly those based on acrylic esters vinyl ethers and iso-butylene, have also been described. Not only impact resistance, but also good resistance to ageing is achieved by the fact that little or no double bonds are contained in the elastomeric polymers. 55
- 25 The present invention relates to an improvement in the production of impact resistant copolymers of styrene and acrylonitrile. It is based on the known use of acrylic esters as elastomeric components in the production of impact resistant styrene polymers. 60
- 30 It is an object of the present invention to prepare moulding materials having good impact resistance at low temperatures as well as a good resistance to ageing. Impact resistant polystyrenes having good impact resistance at low temperatures may be obtained by using butadiene polymers, particularly those having 1,4-cis configuration, as elastomeric components. A preferred polymer of this type is 1,4-cis-polybutadiene. With the good impact resistance at low temperatures achieved, there is of course a worsening in the resistance to ageing which has to be put up with because the double bonds contained in the 65
- 35 [Pric.] 70
- 40 [Pric.] 75

soft component promote oxidative and thermal degradation.

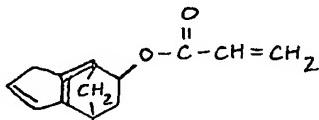
It has already been proposed to use, as elastomeric components, graft polymers which have been obtained by polymerising acrylic esters on to low molecular weight polybutadienes and on to which styrene and acrylonitrile are then grafted. In the case of this rubber also, double bonds remain in the main chain after the grafting reaction.

We have now found that moulding materials based on styrene/acrylonitrile polymers having good impact resistance at low temperatures combined with good resistance to ageing are obtained when they consist of an intimate mixture of:— (A) 15 to 50 parts by weight of a graft copolymer of 10 to 50% by weight of a mixture of styrene and acrylonitrile in the ratio 60:40 to 90:10, which has been polymerised on to 50 to 90% by weight of a copolymer of 2 to 20% by weight of the acrylic ester of tricyclodeceny alcohol and 98 to 80% by weight of an acrylic ester of an alcohol having four to eight carbon atoms; and (B) 50 to 85 parts by weight of a copolymer of styrene and acrylonitrile in the ratio 50:50 to 90:10.

The moulding materials according to this invention accordingly consist of a mixture of components (A) and (B), (A) being the elastomeric component and (B) the component containing the hard and brittle polymer. Component (A) is a graft copolymer in which a mixture of styrene and acrylonitrile has been polymerised on to a copolymer of at least two different acrylic esters, so that the mixture of styrene and acrylonitrile is grafted on to the two acrylic esters.

The component (A) may be prepared as follows:—

First it is necessary to prepare a copolymer of different acrylic esters as backbone material; these esters are (a) acrylic esters of alcohols having four to eight carbon atoms, for example butyl acrylate or ethylhexyl acrylate, and (b) tricyclodeceny acrylate I:—



I

The ratio of the two types of acrylic ester should be 2 to 20% by weight of the cycloaliphatic acrylic ester and 98 to 80% by weight of the acrylic ester of a C₄- to C₈-alcohol. It is self-evident that within the said range of amounts, various acrylic esters of the said groups may be copolymerised (the percentage in each case amounting to a total of 100%).

A mixture of styrene and acrylonitrile is then polymerised on to the copolymer of the different acrylic esters. From 10 to 50% by weight with reference to the final graft copolymer of a mixture of styrene and acrylonitrile should be used for this purpose. The mixture of styrene and acrylonitrile should have a ratio of from 60:40 to 90:10. Copolymerisation of the acrylic esters and the subsequent grafting of the mixture of styrene and acrylonitrile on to the same are preferably carried out in aqueous emulsion. Conventional polymerisation assistants, such as catalysts, regulators and emulsifiers, and also the conventional polymerisation conditions, temperature range and the like are used.

The graft copolymer (A) thus obtained may in some cases already be a mixture of different polymers. This mixture consists of the graft copolymer of styrene/acrylonitrile on the acrylic ester copolymer as the backbone polymer and possibly the copolymer of styrene and acrylonitrile.

The elastomeric component (A) is mixed with the hard component (B). The component (B) consists of a copolymer of styrene and acrylonitrile. The copolymer of styrene and acrylonitrile (the styrene and acrylonitrile units being present in the ratio 50:50 to 90:10) is obtained by conventional methods. Conventional methods include particularly polymerisation in bulk in the absence of substantial amounts of diluents, or by emulsion polymerisation. The copolymer of styrene and acrylonitrile may also be prepared by polymerisation in suspension in methanol in a conventional manner.

The component (A) is preferably mixed with the component (B) by adding the grafted and dried emulsion polymer to the styrene/acrylonitrile copolymer and mixing them in a melt. This may be carried out for example in an extruder or another kneading means.

If the components (A) and (B) are both in the form of aqueous emulsions, mixing may take place by bringing the emulsions together and effecting coprecipitation of the solids contained therein. Finally it is also possible to mix component (A) in the form of an emulsion with component (B) in the form of a solution and to effect coprecipitation, if desired after having added a precipitant.

The moulding materials according to the invention are distinguished by a better resistance to ageing than products containing butadiene. Articles of daily use made from these materials have a good surface gloss and a pale natural colour.

The invention is illustrated by the following Example. The parts specified in the Example are by weight. The production of the components (A) and (B) is not the subject of the present invention.

60

65

70

75

80

85

90

95

100

105

110

115

120

EXAMPLE

- 18 parts of n-butyl acrylate and 2 parts of tricyclodecyl acrylate in 145 parts of water are heated to 65°C while stirring with
 5 an addition of 1.2 parts of the sodium salt of a paraffin sulphonic acid ($C_{12}-C_{14}$) and 0.35 part of potassium persulphate. After the polymerisation has been initiated, a mixture of 72 parts of n-butyl acrylate and 8 parts
 10 of tricyclodecyl acrylate is added during the course of two hours. After all the monomers have been added, the polymerisation mixture is stirred for another hour at 65°C.
 An approximately 40% aqueous polymer dispersion is obtained.
 15 250 parts of this dispersion is mixed with 25 parts of a mixture of styrene and acrylonitrile in the weight ratio 70:30 and 37.5 parts of water and polymerised at 65°C
 20 while stirring. 0.05 part of potassium persulphate and 0.075 part of lauroyl peroxide are added as a polymerisation accelerator. Again an approximately 40% aqueous polymer dispersion is obtained from which the solid product is precipitated by adding a 0.75% calcium chloride solution, washed with water and dried in a current of hot air.
 25 30 parts of the dried polymer powder (A) is mixed in a screw extruder with 70 parts of a copolymer (B) of 70 parts of styrene and 30 parts of acrylonitrile (K-value 65) at a temperature of about 220°C. The product thus prepared may be processed well on conventional injection moulding machines.
 30 35 Articles of daily use having great stiffness, good shock resistance and a glossy surface may be prepared.
 Shock resistance is determined as the mean breaking energy in biaxial stress on test plates
 40 having a thickness of 1 mm. This test is carried out with drop bolt equipment consisting essentially of the following parts: a base plate having guide bars for the drop bolts, a supporting ring (diameter 30 mm)
 45 for the test plates, a number of drop bolts having different net weights and additional weights therefor. The points of the drop bolts are hemispherical in shape and have a diameter of 18 mm.
 50 55 Measurement consists in determining the number of breakages in the case of several spot samples each of ten small plates at various energy levels, i.e. with drop bolts having different weights and being dropped from the same height.

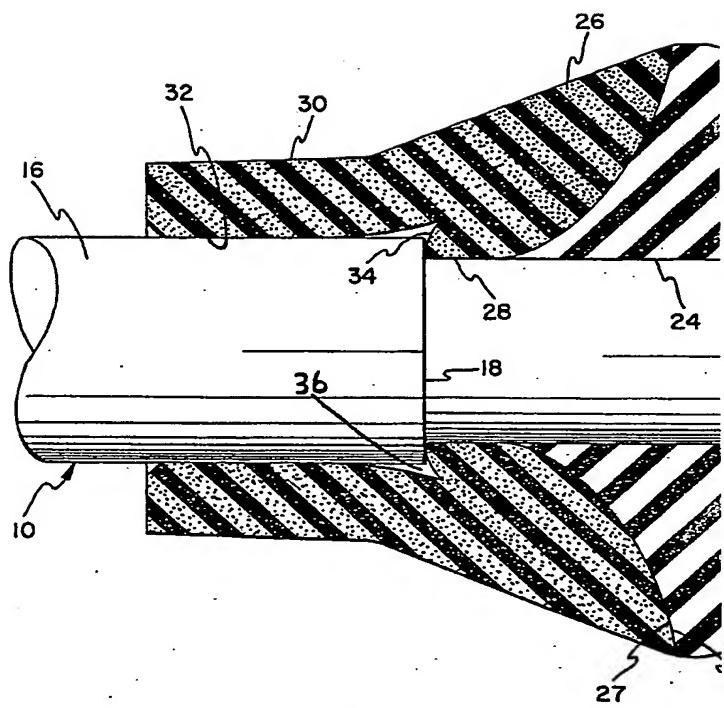
In this way a coordination of the frequency of breakage in % to definite energy values in cm.kg is obtained. If the frequency of breakage be plotted against the energy in a probability curve, a good approximation to a straight line is obtained. The point of intersection of this straight line with the 50% line gives the value for the mean breaking energy.

The product (measured on press moulded circular small plates) has a mean breaking energy of 64 cm.kg.

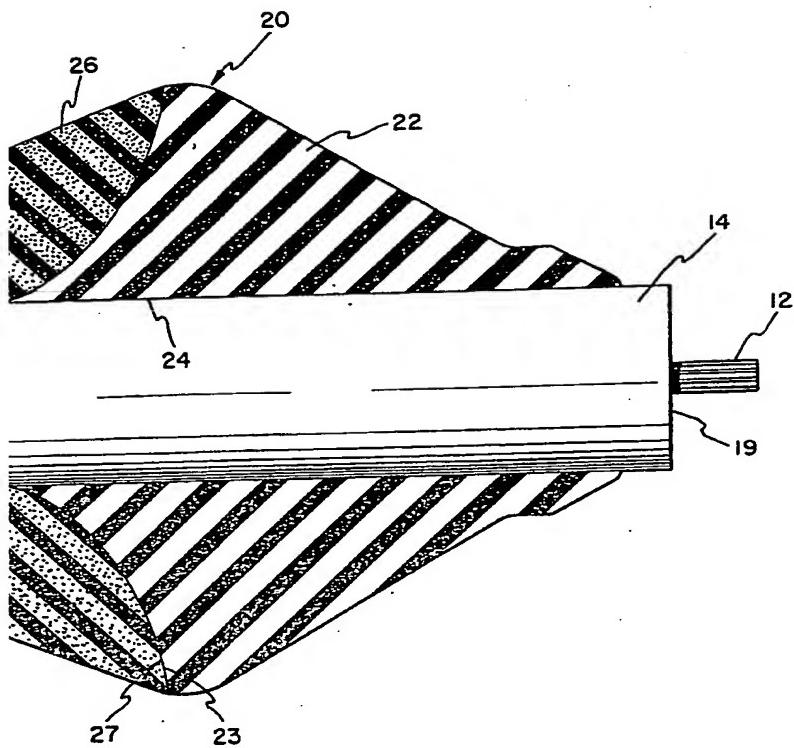
WHAT WE CLAIM IS:—

1. Moulding material comprising an intimate mixture of:—
 (A) 15 to 50 parts by weight of a graft copolymer of 10 to 50% by weight of a mixture of styrene and acrylonitrile in the ratio of 60:40 to 90:10, which is polymerised onto 50 to 90% by weight of a copolymer of 2 to 20% by weight of tricyclodecyl acrylate and 98 to 80% by weight of an acrylic ester of an alcohol having four to eight carbon atoms; and
 (B) 50 to 85 parts by weight of a copolymer of styrene and acrylonitrile in the ratio 50:50 to 90:10.
2. Moulding material as claimed in claim 1 prepared by mixing components (A) and (B) in a melt.
3. Moulding material as claimed in claim 1 or 2 prepared by mixing the components in an extruder.
4. Moulding material as claimed in claim 1 prepared by mixing components (A) and (B) in the form of aqueous emulsions and effecting coprecipitation of the solids contained therein.
5. Moulding material as claimed in claim 1 prepared by mixing a solution of component (B) with an emulsion of component (A) and effecting coprecipitation of the solids.
6. Moulding material as claimed in claim 1 substantially as described in the foregoing Example.

J. Y. & G. W. JOHNSON,
 Furnival House,
 14-18, High Holborn,
 London, W.C.1.
 Chartered Patent Agents
 Agents for the Applicants.



1124912 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of
the Original on a reduced scale*



1124912 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of
the Original on a reduced scale

